USE OF A CHROMIUM STEEL AS RAW MATERIAL FOR CORROSION-RESISTANT SPRING ELEMENTS AND METHOD FOR PRODUCING SAID CHROME STEEL

[0001]   The invention relates to the use of a chromium steel comprising 0.03 to 0.1% of carbon, 0.2 to 0.9% of silicon, 0.3 to 1% of manganese, 13 to 20% of chromium, less than 0.5% of nickel, 0.1 to 1.5% of molybdenum, 0.1 to 0.5% of copper, 0.03 to 0.05% of nitrogen, less than 10 ppm of boron, less than 0.01% of titanium, 0.01 to 0.10% of niobium, 0.02 to 0.25% of vanadium and preferably less than 0.002% of aluminum, remainder iron.

[0002]   Chromium steels with a ferritic or, depending on their nickel content, a ferritic-austenitic microstructure have a high resistance to corrosion and are known in numerous forms.

[0003]   For example, European laid-open specification 1 099 773 A1 describes a ferritic chromium steel containing 0.02 to 0.06% of carbon, up to 1% of silicon, up to 1% of manganese, 11 to 30% of chromium, up to 0.7% of nickel, up to 0.05% of phosphorus, up to 0.01% of sulfur, up to 0.005% of aluminum, and the nitrogen, vanadium and carbon contents of which are matched to one another in a specific way. This steel is very soft and is therefore suitable as a material for stainless deep-drawing sheets with a low anisotropy.

[0004]   Furthermore, European laid-open specification 1 113 084 A1 describes a ferritic chromium steel containing up to 0.1% of carbon, in each case up to 1.5% of silicon and manganese, 5 to 50% of chromium, up to 2% of nickel, up to 2.5% of molybdenum, up to 2.5% of copper, up to 0.1% of nitrogen, up to 0.05% of boron, up to 0.5% of titanium, up to 0.5% of niobium, up to 0.3% of vanadium, up to 0.08% of phosphorus, up to 0.02% of sulfur, up to 0.2% of aluminum, up to 0.3% of zirconium and up to 2.0% of tungsten. The steel is very

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soft and, on account of its good deformability, is likewise suitable as a material for deep-drawing sheets with a defined crystal orientation following rolling deformation and a final anneal at 800 to 1100°C.

[0005]   Finally, US patent 5,178,693 describes a ferritic-austenitic chromium steel containing 0.01 to 0.15% of carbon, up to 1.39% of silicon, 0.1 to 4.0% of manganese, 10 to 20% of chromium, up to 2.5% of molybdenum, 0.1 to 4.0% of copper, up to 0.032% of nitrogen, up to 0.0050% of boron, up to 0.02% of vanadium and up to 0.20% of aluminum. This steel is suitable for the production of thin strip, from which, following a final continuous anneal at 300 to 650°C, leaf springs can be produced by stamping or cutting them out. However, it has emerged that the strip, after the final anneal at the temperature indicated and cooling to room temperature, has high internal stresses which, depending on its thickness, leads to distortion of the stamped parts when they are being stamped out. This is a significant drawback in the case of spring elements, in particular in the case of lamellar springs, since they then still have to be straightened and bent for final shaping. Moreover, if the internal stresses are relatively high, the fatigue strength may drop.

[0006]   Materials used for spring elements require a high linear spring rate, which is determined from the inclination of a force/deflection straight line using the formula

$$R = \delta F/\delta s$$

[0007]   where F is the force and s is the deflection. Furthermore, in the case of spring elements the permissible spring limit stress is a characteristic feature which is calculated, in accordance with DIN 2088 and DIN 2089, from the tensile strength R_m multiplied by a constant. Depending on the spring geometry and application, this constant is from 0.4 to 0.7 depending on the individual

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circumstances.

[0008]   Although carbon steels with carbon contents of up to 1% have high R_m values after a heat treatment and therefore also allow high limit stresses, their corrosion resistance, and in particular their resistance to rust, is low. This is a serious drawback, since spring elements are generally exposed to humid air and are also in widespread use in the chemical industry. Consequently, austenitic steels are more suitable, on account of their high corrosion resistance. However, these steels require a relatively high level of expensive alloying elements, such as in particular nickel. The same is also true of precipitation-hardenable austenitic steels, which contain aluminum, titanium or niobium in order to improve their strength.

[0009]   Moreover, for health reasons, nickel-containing steels are not suitable for objects which come into contact with the human skin, for example jewellery.

[0010]   Martensitic chromium steels are less expensive but have the drawback of poorer cold-workability, and can therefore only be processed to form spring elements in the annealed state. The springs produced therefrom require an anneal or hardening treatment at high temperatures and subsequent tempering. The hardening of the individual parts is associated with high costs and, for reasons of quality, requires a hardness test for final inspection, and consequently the cost benefit derived from the elimination of expensive alloying elements is lost again. Moreover, in the case of martensitic chromium steels there is a risk of islands and nests of chromium carbides forming in the microstructure, leading to a deterioration in the corrosion resistance.

[0011]   Even a coating is unable to achieve an extensive, in particular prolonged improvement in the corrosion resistance, since coatings of this type

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have to have a very low thickness and lose their protective action as a result of wear or damage. Moreover, in the case of metallic coatings, local elements which lead to increased corrosion may form at damaged locations. The risk is particularly high in the case of spring elements, since such elements are often provided with stamped-out portions and spot welds or are arranged in metallic clamping guides in order for their position to be fixed.

[0012]   The invention is aimed at improving the spring properties, characterized by the tensile strength and dimensional accuracy of spring elements made from a corrosion-resistant steel.

[0013]   To achieve this, the invention proposes the use of a ferritic chromium steel comprising 0.03 to 0.1% of carbon, 0.2 to 0.9% of silicon, 0.3 to 1% of manganese, 13 to 20% of chromium, less than 0.5% of nickel, 0.1 to 1.5% of molybdenum, 0.1 to 0.5% of copper, 0.03 to 0.05% of nitrogen, less than 10 ppm of boron, less than 0.01% of titanium, 0.01 to 0.10% of niobium, 0.02 to 0.25% of vanadium, remainder iron.

[0014]   A ferritic chromium steel comprising 0.03 to 0.08% of carbon, 0.2 to 0.9% of silicon, 0.4 to 0.8% of manganese, 15 to 18% of chromium, less than 0.2% of nickel, in each case 0.1 to 0.5% of molybdenum and copper, 0.03 to 0.05% of nitrogen, less than 8 ppm of boron, less than 0.005% of titanium, 0.01 to 0.05% of niobium and 0.05 to 0.20% of vanadium, remainder iron, is particularly suitable.

[0015]   The invention combines the high corrosion resistance of the ferritic chromium steels with the high tensile strength of high-alloy spring steels; it makes use of the following discoveries:

[0016]   Higher annealing temperatures, in particular annealing temperatures

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of from 1000 to 1200°C, can be used as a result of the titanium content being reduced to less than 0.005%. Under these conditions, no titanium carbides and/or titanium carbonitrides are formed as MX precipitations which have an embrittling action. These compounds would preferentially form at the grain boundaries, thereby preventing or making more difficult subsequent cold-working.

[0017]   On account of the higher annealing temperature, it is possible to increase the dissolution of the carbides and/or carbonitrides to such an extent that - on account of the absence of precipitation nuclei of titanium carbide or titanium carbonitride - after quenching a very high proportion of alloying elements remains metastable in solution. This higher level of dissolved or metastable-dissolved elements and/or precipitations ought to be responsible for the excellent cold-workability and for the high work hardening of the steel in accordance with the invention.

[0018]   Furthermore, the limiting of the titanium compound combined, at the same time, with micro-alloying with the elements vanadium and niobium, particularly advantageously prevents titanium-containing MX precipitations acting as isomorphic nuclei, i.e. nuclei with an identical lattice structure, for common, coherent vanadium and niobium precipitations. Since vanadium is preferentially precipitated in nitride form, whereas niobium is preferentially precipitated as 50:50 carbonitride, the growth kinetics of these precipitations are different. The increase in strength resulting from a heat treatment at temperatures from 100 to 300°C is attributable to the growth of metastable precipitations.

[0019]   To avoid relatively insoluble borides, the boron content should be below 10 ppm, and the aluminum content should be below 0.002%.

[0020]   Furthermore, the steel may also contain less than 0.002% of aluminum.

[0021] In the proposed steel, the carbon and nitrogen and/or niobium, vanadium and titanium contents are preferably matched to one another as follows:

$$(\%C)/(\%N) = 0.8 \text{ to } 2.0$$
$$[(\%Nb) + (\%V)]/10(\%Ti) = 5 \text{ to } 17.$$

[0022] The steel according to the invention is distinguished by an extraordinarily high tensile strength, an excellent cold-formability and high corrosion resistance; it has a very fine-grade microstructure and allows high temperatures to be used in a solution anneal without the risk of grain boundary embrittlement as a result of carbides and/or carbonitrides. After a solution anneal of this type, which is atypical for ferritic steels, preferably for one to fifteen minutes at 1000 to 1200°C, these compounds remain metastable in solid solution and allow optionally multistage cold-working. The cold-working is preferably followed by final heating at 100 to 400°C, preferably at most 300°C, for ten to fifteen minutes.

[0023] In detail, the chromium steel according to the invention may be cold-worked in the form of round wire with a decreasing cross section of up to 40%, preferably up to 35%, and a solution anneal may then be carried out in order to substantially eliminate the carbide and carbonitride precipitations, with subsequent quenching. When it is in the state in which it has been cold-worked, solution-annealed and quenched, the steel or wire has an excellent cold-workability, which can be improved still further by a further cold-working with decreases in cross section of up to 65%, for example 50%. The strength of the steel then already exceeds that of a conventional cold-rolled spring steel strip in accordance with DIN 17 222 and DIN 17 224, with R_m values of from 1150 to 1500 N/mm^2 for steel grades Ck 55, Ck 67, Ck 101 and 50CrV4.

[0024] The microstructure of the heat-treated and cold-worked steel according to the invention, with a grain size of less than 20 µm, is extraordinarily fine-grained, as is clear from the microstructure image shown in Fig. 2, compared to the starting microstructure, which is already fine-grained, shown in Fig. 1. The microstructure image shown in Fig. 2 reveals that the microstructure is ferritic but contains a small quantity of transformation microstructure constituents (dark areas), which must be martensite, which has the effect of increasing strength.

[0025] Finally, the steel may also be subjected to a third cold-working with a degree of deformation of up to 12%, in which a wire with a rectangular cross section is produced from the round wire in order to reduce the grain size to less than 15 µm.

[0026] Irrespective of the number of deformation stages, the steel should be age-hardened at a low temperature, preferably at 100 to 400°C, more preferably at at most 300°C, in order to further increase the tensile strength.

[0027] This age-hardening at a very low temperature is preferably carried out under the action of a stress and/or a surface pressure of from 20 to 100 N/mm^2 and serves to eliminate any internal stresses, in particular transverse stresses.

[0028] The steel is particularly suitable for use as a material for producing leaf springs, spring rails for windscreen wipers, reed lamellae for textile machines, oil stripper rings for internal combustion engines and sealing lamellae for hydraulic installations. On account of its low nickel content, moreover, the steel has a very good compatibility with the skin and is therefore also suitable as a material for bracelet and strap clasps, bracelets and straps and items of use with a low nickel release rate in accordance with EU directive 94/27 EC dated June 30, 1994 (cf. AJ L 188/1), which stipulates a release rate of less than 0.5 $µg/cm^2$/week,

whereas in the case of a conventional 18/8 chromium nickel steel the nickel release rate may reach up to 100 $\mu g/cm^2$/week.

[0029] The steel according to the invention has a corrosion resistance and spring properties which, measured on the basis of the tensile strength, reaches the level of high-alloy austenitic steels, such as X5CrNiMo18,10.

[0030] The steel has a ferritic microstructure with niobium and/or vanadium carbides or niobium carbides; however, on account of its titanium content of less than 0.01%, preferably less than 0.006%, it does not contain any titanium-containing precipitations. Specifically, tests have revealed that the titanium carbides are retained during the solution anneal and are not dissolved. To this extent, the titanium carbides behave differently than the carbides of vanadium and niobium, which dissolve. Moreover, the titanium carbides cause grain boundary precipitations which have an embrittling action at high annealing temperatures, and consequently the titanium content should be below 0.01%, preferably below 0.006%, even better below 0.004%.

[0031] The invention is illustrated by way of example in the block diagram presented in Fig. 3; it is explained in more detail below on the basis of comparative tests.

EXAMPLE 1

[0032] A round wire made from steel A1 in accordance with Table I with a diameter d_0 was rolled down to a diameter d by means of driven hard-metal disks. The degree of deformation was calculated for each test as a relative dimension change ε using the formula

$$\varepsilon = 100 \bullet \Delta d/d_0$$

from the cross-section difference $\Delta d = d_0 - d$.

[0033]   In each series of tests, the adjustment of the hard-metal disks was altered toward an increasing reduction in cross section, until surface defects, in particular surface cracks, occurred or the adjustment forces or the rolling forces acting on the hard-metal disks reached a predetermined limit level.

[0034]   The degrees of deformation are summarized in Table II, in which ε_1, ε_2 and ε_3 denote the degrees of deformation of the first, second and third cold-working steps.

[0035]   The round wire which had been cold-worked with degree of deformation ε_1 was heated in a continuous annealing furnace under shielding gas with a dew point below -65°C to the temperature T1 shown in Table II. On leaving the heating zone of the furnace, cold shielding gas was flushed around the solution-annealed round wire in order to avoid oxidation, and the wire was then quenched with water and dried in air.

[0036]   During a final heat treatment following a cold-working operation, the round wire made from steel A1 was subjected to a final anneal in a continuous process in a furnace provided with driven rolls at both the entry side and the exit side. It was in this way possible to heat the round wire under tensile stress in a heating tube, with the aid of infrared rays, at the temperatures T2 shown in Table II. The rotational speeds of the driven rolls were controlled in such a way during the heating that the round wire was under a tensile stress of 20 N/mm^2 and a heat treatment of 35 min resulted from the drawing speed.

[0037]   The round wire which had been heat-treated in this way was processed to form spring elements. Investigations revealed only a slight scatter in the spring properties.

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EXAMPLE 2

[0038] To produce compression and/or oil stripper rings or piston rings for internal combustion engines, a round wire made from the steel A2 in accordance with Table I was firstly deformed with a degree of deformation of $\varepsilon_1 = 23\%$ to form a flattened wire with a square cross section. The flattened wire was then heated under shielding gas in a continuous process in a heating furnace to 1065°C and then quenched in water. After intermediate drying, the wire was deformed with the aid of a cartridge rolling device with a degree of deformation of $\varepsilon_2 = 43\%$ to form a preliminary profiled section. This was followed by further working with the aid of a drawing die with a degree of deformation of $\varepsilon_3 = 6\%$ to produce the predetermined piston ring cross section.

[0039] The finished wire had a tensile strength of 1620 N/mm^2 with a residual elongation of 3%.

[0040] The second heat treatment (final heating) is not absolutely imperative, since, for example, piston rings with a slight ovality of up to a few μm, in the installed state, on account of their ovality are under a force fit or mechanical stresses, but these are quickly broken down after the engine has started to be used as a result of the combustion heat which occurs.

[0041] Two conventional chromium steels B1 and B2 with a composition which meant that the carbon was stably bonded by titanium as titanium carbide are compared with the steels A1 to A3 according to the invention in Table I. The data in Table II reveals that in the case of these comparison steels, the maximum permissible annealing temperature of 800°C from the specialist literature relating to ferritic chromium steels must not be exceeded, since otherwise grain boundary embrittlement occurs, making subsequent cold-working extremely difficult or even impossible. By contrast, the chromium steels according to the invention, as shown

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by the data for the test steels A1 to A3, can be annealed at considerably higher temperatures and accordingly have better cold-working properties and in particular an advantageous performance during low-temperature final annealing. This is true in particular if the titanium, niobium and vanadium and/or carbon and nitrogen contents are matched to one another in accordance with the invention.

[0042]   It is clear from the data given in Table I that the steels according to the invention A1 to A3 reach a tensile strength (Rm1) of up to 1590 N/mm^2 as the temperature T1 for the first heat treatment and a subsequent cold-working increases. At lower temperatures of, for example, 850°C, it is impossible to achieve any significant increase in strength even after cold-working, as revealed by the data from the two tests 1 and 2. Tests 14 to 16 for the conventional steel B1 have the same characteristics. This means that the temperature used during the solution annealing should be over 850°C and should preferably be 1000 to 1200°C.

[0043]   The data for tests 3 to 13 using the chromium steels A1 to A3 according to the invention reveal the importance of a sufficiently high temperature during the first heat treatment in conjunction with cold-working in accordance with the invention and, furthermore, demonstrate how much the tensile strength can be increased with the aid of the second heat treatment at a temperature of up to 300°C. In this respect, test 10 reveals that a heat treatment at 350°C is no longer associated with an increase in strength.

[0044]   The high strength values demonstrated by the data of tests 1 to 13 for the steels according to the invention can be attributed to microstructure precipitations which result during the cold-working and heating in accordance with the invention (cf. Fig. 2). This applies in particular to the quenching from the high temperature of the first heat treatment (solution anneal). It is particularly noticeable in this context that the solution anneal (at temperatures from 1000° to

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1200°C) at high temperatures is not associated with grain boundary embrittlement caused by carbides and/or carbonitrides.

[0045]   The process steps according to the invention, by contrast, in the comparison steels B1 and B2 do not lead to any significant improvement in the tensile strength, as shown in tests 14 to 23. Although cold-working with degrees of deformation of up to 40% is still possible after a first heat treatment at 850°C (tests 15 and 16), this does not involve any significant increase in strength. At higher annealing temperatures of over 1000°C, by contrast, grain boundary embrittlement, which is typical of ferritic chromium steels, occurs, making subsequent cold-working impossible.

Table I

Alloy No.	Invention	Cr (%)	Si (%)	Mn (%)	C (%)	N (%)	Ni (%)	Mo (%)	Ti (%)	Nb (%)	V (%)	Cu (%)	B (ppm)
A1	Yes	16.6	0.5	0.49	0.07	0.048	0.39	0.12	0.002	0.16	0.14	0.11	3
A2	Yes	18.3	0.42	0.63	0.05	0.052	0.25	0.25	0.001	0.15	0.20	0.21	5
A3	Yes	18.7	0.46	0.63	0.035	0.038	0.21	0.32	0.001	0.17	0.10	0.31	5
B1	No	18.0	0.52	0.38	0.043	0.021	0.52	0.02	0.18	0.04	0.06	0.12	15
B2	No	18.7	0.61	0.52	0.081	0.029	0.46	0.06	0.12	0.06	0.09	0.34	12

Table II

Alloy No.	Test No.	ε1 (%)	T1 (°C)	ε2 (%)	ε3 (%)	Rm1 (N/mm²)	Deformability	T2 (°C)	Rm2 (N/mm²)
A1	1	10	850	30	none	680	good	none	-
A1	2	10	850	30	15	750	good	120	745
A1	3	10	1050	40	15	1175	good	120	1220
A1	4	35	1050	30	10	1425	good	none	1485
A1	5	35	1050	40	10	1480	good	120	1560
A2	6	35	1050	50	15	1495	good	150	1650
A2	7	35	1100	50	10	1540	good	150	1695
A3	8	35	1120	40	15	1515	good	none	-
A3	9	35	1120	50	15	1535	good	100	1620
A3	10	35	1120	60	15	1550	good	150	1680
A3	11	35	1120	70	15	1590	good	250	1710
A3	12	35	1120	70	15	1590	good	350	1490
A3	13	35	1120	70	15	1590	good	450	1405
B1	14	10	850	15	15	690	good	150	690
B1	15	25	850	30	15	830	good	150	835
B1	16	25	850	40	-	1150	poor	150	1145

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B1	17	25	1000	10	-	990	poor	150	995
B1	18	35	1050	-	-	-	very poor	-	-
B2	19	35	1000	10	-	620	poor	150	630
B2	20	35	1000	18	-	675	poor	150	670
B2	21	25	1050	-	-	-	poor	-	-
B2	22	35	1050	-	-	-	poor	-	-
B2	23	25	1100	-	-	-	very poor	-	-

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